

# SCIENCE FOR CERAMIC PRODUCTION

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## EFFECT OF GRANULE SIZE ON THE STRUCTURE OF NANOPOROUS CERAMICS BASED ON ORGANOSILICON POLYMER

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Porosity in nanoporous ceramics produced by pyrolysis of organosilicon polymer at a temperature of 600°C was investigated using the BET method. Samples were molded from fractionated granules produced by single or double milling in a planetary mill of a polymer previously solidified and heat-treated at 200°C. Specific surface area depending on nanopores sharply decreases after the granules reach a size over 250  $\mu\text{m}$  in single milling and over 1000  $\mu\text{m}$  in double milling. An explanation for these facts is given in the context of synergism.

Ceramics with nanopores find increasing applications in separation processes as molecular sieves for chemical processes, filters for gas purification at high temperatures, sensors, etc. Nanoporous ceramics can be produced by pyrolysis of organosilicon polymers [1]. In making catalysts or sensors, nanoporous materials need to have larger pores to allow gases to easily penetrate inner parts of the sample. To ensure high strength, the larger pores should have similar sizes and be evenly distributed in the volume of material, i.e., the material should have a bimodal size distribution of pores.

According to the data in [2], micropores in nanoporous ceramics were formed due to inhomogeneity of polymer developed in its pre-pyrolysis treatment. Inhomogeneities were produced by two methods. According to the first method, they emerged in emission of gases from the polymer during its pre-pyrolysis treatment. After pyrolysis of polymer at 600°C, samples with micropores and nanopores and a specific surface area of 41  $\text{m}^2/\text{g}$  were obtained. According to the second method, heterogeneities in polymer were created by poor mixing with the curing agent. After heat treatment at 600°C, samples with micro- and nanopores were obtained as well and had a specific surface area of 229  $\text{m}^2/\text{g}$ . Heterogeneities developed in pre-pyrolysis treatment acted as an internal controlling signal in the evolution of the material structure in the course of pyrolysis of polymer. However, these results had extremely low reproducibility, since the system possessed a multistability with the stable states significantly differing in their properties, whereas the system itself was unstable [3].

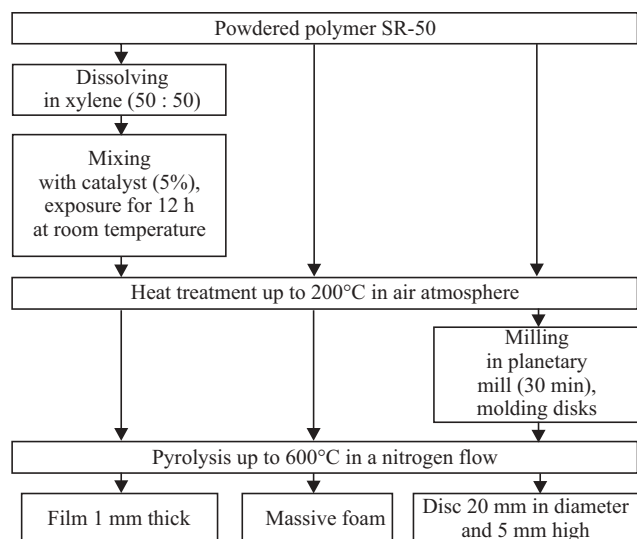
Ceramic technologies frequently use granulation of powder before molding as an inner controlling signal that influences the evolution of the material structure. This makes it possible to obtain articles with a more uniform density.

The purpose of the present study was to develop a stronger inner controlling signal by granulation of polymer after pre-pyrolysis treatment. Granules were obtained in milling a polymer heat-treated at 200°C in a planetary mill for 30 min. The granules were screened on sieves into the following fractions ( $\mu\text{m}$ ): < 25, 25 – 45, 45 – 90, 90 – 180, 180 – 250, 250 – 355, 355 – 1000, 1000 – 2000, and > 2000. Part of large granules sized over 355  $\mu\text{m}$  were again milled in the same conditions and again screened on sieves into the same fractions. These granules were used to mold cylindrical samples 20 mm in diameter and 5 mm high at a pressure of 30 MPa, which were then subjected to pyrolysis at a temperature of 600°C.

The precursor polymer was polymethylsiloxane SR-350 produced by the General Electric. This polymer is solid at room temperature, clear, has density around 1.08  $\text{g}/\text{cm}^3$ , and contains one methyl and one hydroxyl group per silicon atom that makes part of the chain – Si – O – Si –.

In preliminary studies the specific surface area of samples prepared as thin film, massive foam, or molded from granules was measured using the BET method. The production of film and massive foam is described in [2]. In preliminary experiments granules for making samples were not screened into fractions. The conditions of sample preparation are shown in Scheme 1. Cross-linking of polymer chains (polymerization) was carried out at room temperature using

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**Scheme 1.** Scheme of sample preparation.

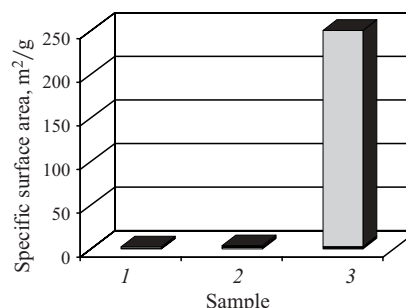
the main catalyst (Dynasylan DAMO  $C_8H_{22}N_2O_3Si$  of company ABCR).

Samples underwent prepyrolysis treatment in the following conditions: temperature was raised at a rate of 60 K/h with 2-hour exposures at 80, 120, and 200°C and then lowered at a rate of 60 K/h. The pyrolysis of the polymer to transform it into ceramics was carried out in a flowing nitrogen medium under the following conditions: temperature was raised at the rate of 120 K/h up to 500°C and then at a rate of 30 K/h to a final temperature of 600°C, after which the samples were exposed for 4 h and cooled at the rate of 120 K/h.

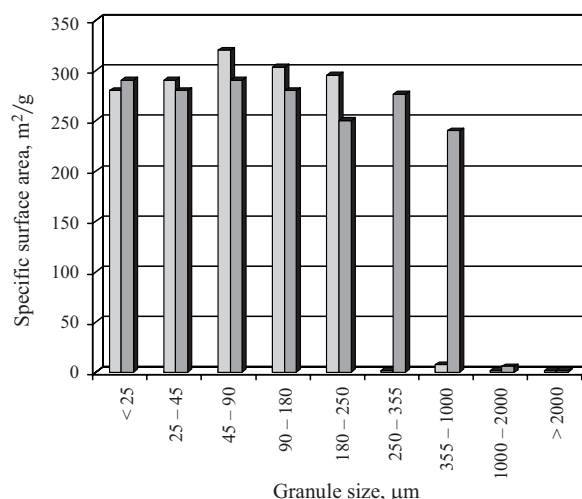
In the second series of experiments the powder was screened into the specified fractions before molding samples. The fractions were prepared from powder milled once or twice in a planetary mill. Granules sized over 355  $\mu m$ , whose content in the powder after a single milling amounted to 48%, were subjected to repeated milling. Pyrolysis of the polymer for making ceramics was carried out in accordance with the specified conditions.

The specific surface area of samples was measured using the BET method on a Gemini meter. The IR spectrum was registered with a BIO-RAD FTS-60A spectrometer. The microhardness of granules was determined using the Vickers method (Mucke 1).

In preliminary experiments a large specific surface area that was mainly due to nanopores ( $245 \text{ m}^2/\text{g}$ ) was registered only in samples prepared by molding granules obtained by milling (Fig. 1). The specific surface area of samples produced from granule after single and double milling is shown in Fig. 2. It can be seen that as the granule size increases above a certain level, the specific area of samples significantly decreases. This shows that such samples contain very few nanopores. In granules after single milling this occurred after a size of 250  $\mu m$  and in granules after a double milling



**Fig. 1.** Specific surface area of samples: 1) film; 2) massive foam; 3) molded disks.

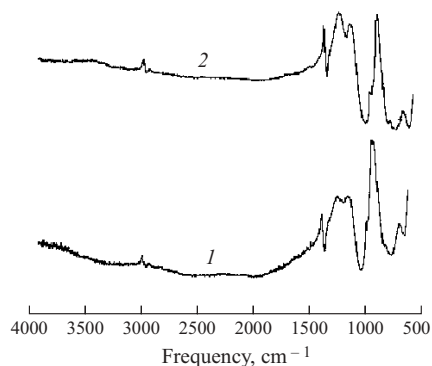


**Fig. 2.** Specific surface area of samples based on fractionated granules after single (left) and double (right) milling.

after a size of 1000  $\mu m$ . The maximum specific surface area was registered in samples produced from granules sized 45 – 90  $\mu m$ . In samples made of granules subjected to single milling it reached  $325 \text{ m}^2/\text{g}$ , and after double milling it reached  $296 \text{ m}^2/\text{g}$ .

IR spectra were recorded in powders with granule size below 25  $\mu m$  prepared by single and double milling (Fig. 3). It can be seen that the spectrum of powder produced by double milling has a decreased peak at  $766 \text{ cm}^{-1}$ , which is interpreted as vibration of the bond  $\gamma_s \text{ Si} - \text{CH}_3$  compared to the double peak at  $1020 - 1110 \text{ cm}^{-1}$  correlating with the bond  $\gamma_{as} \text{ Si} - \text{O} - \text{Si}$  [4]. This is evidence of the mechanochemical reactions in the pyrolysis of the polymer in vibration milling, and their consequences become more evident with increasing duration of milling.

The Vickers microhardness was determined on granules sized 90 – 180  $\mu m$ . The average result was HV 8.5 and HV 11.6 for powders milled once and twice, respectively. This shows that after the second milling the strength of the powder significantly increases. The reason for that is apparently the formation of stronger  $-\text{Si} - \text{O} - \text{Si}-$  bonds, as a consequence of mechanochemical decomposition of polymer.



**Fig. 3.** IR spectra of molding powders with granule size below 25  $\mu\text{m}$  produced by single (1) and double (2) milling.

Nanopores arise in material due to emission of gaseous products of pyrolysis toward the surface of the material. The temperature interval between 500 and 900°C is the most significant for producing ceramics with a high specific area. On a further increase in temperature, open nanopores disappear due to sintering or are transformed into sealed pores, which decreases the specific surface area [5 – 9].

The obtained results can be accounted for as follows: Under a molding pressure of 30 MPa the granules for the most part are not destroyed and act as the inner controlling signal influencing the evolution of the material structure in the course of pyrolysis. In doing so, open pores are formed between the granules, which facilitates the release of gases formed in pyrolysis from the granules. However, after the granule size grows to a certain critical value, the gases released from the central parts of the granule in pyrolysis do not have time to reach the surface and are forced to accumulate inside the granule. The gases from inside exert pressure on the adjacent parts of the granule and facilitate its compaction. In this way the nanopores disappear or are transformed into sealed nanopores. This is the reason why with a single milling the porosity sharply decreases after the granules exceed the critical size of 250  $\mu\text{m}$ .

The samples that were not made of granules had very low porosity. As a consequence of self-organization, the polymer in them also disintegrates into blocks [2]. In the given conditions of thermal treatment, the size and gas permeability of the blocks were such that the gases did not have time to exit from the central parts, which produced a decrease in nanoporosity and, accordingly, in the specific surface area of material.

After a double milling, pyrolysis in the polymer proceeded more completely than after a single milling, and the polymer structure in the granules changed. This agrees with the IR spectroscopy data. The formation of stronger –Si–O–Si– bonds facilitates an increase in the microhardness of granules. Channels for gas emission might have emerged in granules at the microlevel and the nanolevel. After the granule size reaches 1000  $\mu\text{m}$ , a sharp decrease in porosity is registered as well. However, two-time milling in-

creases the critical size from 250 to 1000  $\mu\text{m}$ , compared with one-time milling.

The higher specific surface area (see Fig. 2) of the samples obtained from granules after one-time milling than those made of granules after double milling with the same granule size (except for granules sized below 25  $\mu\text{m}$ ) can be attributed as well to the mechanochemical reaction in milling. Apparently, the disturbance of the polymer structure and the removal of organic radicals occurring under a mechanochemical impact leads to a certain decrease in the amount of nanopores formed in pyrolysis.

In the particular case granulation acted as the internal controlling signal affecting the evolution of the material structure [10]. The effect was produced both by granule sizes and their properties. The inner controlling signals (prehistory) make it possible to modify the evolution of the system if their value exceeds the level of uncontrollable signals (noises).

Thus, an efficient method for getting a bimodal distribution of pores while preserving nanoporosity is the use of polymer granules prepared by milling in a planetary mill. The granule properties are determined by mechanochemical reactions proceeding in the polymer. The granule size in this case should not exceed a certain critical size, after which the nanoporosity sharply decreases.

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